PROPERTY CONTROL OF HIGH-PURITY TITANIUM OXIDE BASED ON THE
VAPOR PHASE OXIDATION METHOD
[Kiso Sanka Ho ni Yoru Ko Jundo Sanka Chitan no Tokusei Seigyo]

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The prospect of controlling the powder properties of a case
where a high-purity titanium oxide is synthesized based on the
vapor phase oxidation method as a perovskite feed material for
providing electronic materials was investigated. The method for
manufacturing titanium oxide by means of vapor phase oxidation is
a method wherein titanium oxide particles are synthesized by
reacting a high-temperature titanium tetrachloride with oxygen.
Conditions for controlling powder properties on such an occasion
were calculated by means of pilot experiments.

As a result, it was ascertained that a 100% rutile can be
synthesized by adding, as a rutile accelerator, water vapor and
that a 100% anatase can be synthesized by controlling the reaction
temperature at a low level. It is essential, from the standpoint
of generating homogeneous particles, to induce a combustion
reaction at the turbulent flow diffusion rate-determining step,

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whereas it became possible, by varying this diffusion rate, to control the average particle size from 0.20 μm to 0.52 μm.

These fundamental experiments have revealed that it is possible to continuously produce, as an electronic ceramic feed material, a titanium oxide powder which is high in purity & homogeneous and bears a singular crystalline tissue wherein flocculation is inhibited & a particle size suitable for a targeted application.

Preface

High-purity titanium oxides are being used as feed materials for providing perovskite-type oxides, which are electronic ceramics, since their compositions & tissues can be controlled with ease.

Attempts were made in the previous report (Go, et al., 1996) to develop & manufacture such high-purity titanium oxides based on the vapor phase oxidation method and to quantitatively analyze synthesizing conditions. As a result, a fine & homogeneous titanium oxide powder of an extremely high purity bearing a particle size of 0.24 μm was successfully obtained.

An attempt were then made to evaluate titanium oxide as a feed material for providing barium titanate, which represents

foundations of various dielectric, piezoelectric, and/or semiconductive elements.

In a case where a barium titanate baking process is considered, the crystalline tissue obtained as a result of a roasting reaction with $BaCO_3$ should theoretically become finer as the sizes of TiO_2 particles decrease, as a result of which the properties of the barium titanate should become improved, and furthermore, it may justifiably be predicted that it will become possible, by reducing the particle size, to up the reactivity in the course of a sintering reaction and to lower the baking temperature. As a matter of fact, extremely favorable performance results were obtained within a laboratory baking furnace. It was impossible, however, to effectively control a baking reaction within a baking furnace of an actual production scale due to the pervasion of a temperature distribution, as a result of which performance aggravations were acknowledged instead. A favorable reactivity can paradoxically be expressed by a wayward reaction tendency & the generation of crude barium titanate crystals, etc., and thus, it has been ascertained that production furnaces of the prior art are difficult to control.

In-between rutile & anatase forms, which differ in reactivity due to their respective crystalline structures, furthermore, the reactivity of the latter is higher. The powder obtained in the

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previous report was a mixture of the crystalline structures of both (70% rutile & 30% anatase), and the possibilities of effects of the compositional irregularity on performances cannot be ruled out.

It can be surmised from the foregoing observations that property controls are necessary for practically providing high-purity titanium oxides, and manufacturing conditions were estimated by conducting experiments in a pilot plant of an industrial scale. The following goals are sought in this context:

①: To synthesize particles bearing as broad a size distribution as possible by encompassing both fine & crude particles;

②: For the primary particle sizes of the respective particles to be homogeneous and for their particle size distribution to be narrow;

③: For the flocculation to be minimal and for the development of secondary particles to be absent;

④: To synthesize crystalline tissues of both rutile & anatase;

⑤: For the shapes of particles to be uniform and, if possible, to provide a powder comprising of spherical particles bearing excellent dispersibility & fluidity in a bulk state.

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The properties of titanium oxides are greatly affected by impurities (Inorganic Material Research Institute, 1979). Since a titanium oxide of a high purity can be synthesized by using the present apparatus based on the CVD method, particle sizes & tissue generation mechanisms can be studied under conditions impervious to effects of impurities.

There exist a handful of extant reports on crystalline tissues of titanium oxides on beaker experiment scales, although no reports under conditions of actual production scales are known.

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Thermal & fluid mechanical phenomena associated with beaker experiments utterly differ from their counterparts under production conditions. The results of extant reports almost exclusively pertain to a case where a reaction gas is [illegible] with a carrier gas within a laminar flow and where a reaction is induced within a reaction tube of the external heating format, as in many CVD embodiments. In the present report, an apparatus similar to that of the previous report is used, and a reaction is induced in a veritable turbulent flow diffusion combustion state without using a carrier gas. The residing time within the reaction tube is therefore extremely brief, namely approximately 0.1 ~ 0.4 s. The objective hereby sought is to obtain rationales

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that can be applied to the fundamental design of an apparatus of an industrial scale, scale upgrade, & operative conditions.

1. Apparatus

1.1. Abstract of apparatus

An overall flow of the apparatus is shown in Fig. 1. Its constitution is utterly identical to that of its counterpart of the previous report (Go, et al., 1996) except that a pure water evaporator is orchestrated at a stage anterior to an oxygen preheater.

A high-purity titanium tetrachloride is vaporized within the evaporator, and its temperature is set at 160°C. The resulting vapor is preheated at 900°C ~ 1,100°C. Pure oxygen, on the other hand, is likewise preheated at 900°C ~ 1,100°C, and these gases are fed into a reaction tube. The titanium tetrachloride becomes oxidized within the reaction tube, as a result of which fine particles of titanium oxide & gaseous chlorine become generated.

$$TiCl_4 + O_2 \rightarrow TiO_2 + 2Cl_2 \ ... \ (1)$$
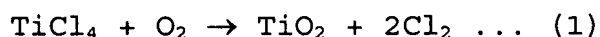
The titanium oxide & chlorine thus generated are cooled by mixing the same with air, and after fine titanium oxide particles have been collected, the chlorine is guided into a [illegible] column and thus removed.

A powder storage tank underneath the collector also serves as a dechlorinating mechanism, whereas after it has been detached from the collector, the internalized powder is heated by blowing a hot air, and the chlorine is removed by desorbing the chlorine adsorbed on the particles or by decomposing a trace of the yet-to-be-reacted chloride. [Said collector is?] substituted with an auxiliary collector before & after the commencement of the reaction and at the time of termination for avoiding the migration of a defective powder.

As far as the scale of this apparatus is concerned, the titanium tetrachloride feeding rate is 100 kg/h, which is tantamount to approximately 1 t/day in terms of daily titanium oxide productivity.

1.2. Reaction tube

To begin with, a property control experiment was conducted within a reaction tube made of quartz, as Fig. 2 indicates. This reaction tube, however, is incapable of perpetuating constant reaction conditions for even several minutes due to the precipitation of the generated titanium oxide, and therefore, a continuous reaction was induced within a water-cooled reaction tube made of graphite in consideration of the sedimentation, as in the previous report.

Attempts were made, from standpoints of homogenizing particle sizes & performances and of inhibiting the progresses of [illegible] sintering, etc. as much as possible, to satisfy the three fundamental conditions mentioned in the previous report, namely, ①: The establishment of nozzle conditions capable of forming a turbulent flow reaction [flame?]; ②: The pervasion of a turbulent flow within the reaction tube; and ③: The designation, as the reaction tube length, of the span of a reaction zone required for the achievement of a stoichiometric state.

2. Experiments & results

2.1. Titanium tetrachloride feed material

A purified titanium tetrachloride of a high purity was used as a titanium tetrachloride feed material, whereas its impurity is shown below:

$TiCl_4$ > 99.9 wt%;

Fe, V, Al, Sn, Pb, As, Mn, Mg, Ca, Ni, Co, & Cd < 0.0003 wt%;

Si & S: < 0.0005 wt%.

The impurities serve, in terms of crystalline structures, either as accelerators or inhibitors for anatase or rutile and also contribute to the generation of crystal nuclei, whereas their effects can be avoided by using high-purity products.

2.2. Crystal control

The Gibbs' standard free energy ΔG' pertaining to the generation of titanium oxide and the enthalpy variation Δ?' accompanying the phase transition of titanium oxide are shown respectively in Fig. 3 & Fig. 4 (Chase, et al., 1975; S??ll and Ptophet, 1971). As Fig. 3 indicates, there is no

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significant difference between anatase & rutile in terms of the Gibbs' standard free energy of the reaction, and rutile is slightly more stable at any temperature. This transition into rutile, furthermore, is irreversible. As has been demonstrated in the previous report (Go, et al., 1996), an anatase-mixed crystal inclusive of abundant rutile becomes obtained as a result of the reaction of oxygen with a heated titanium tetrachloride. The anatase of the generated titanium oxide can be quickly transformed into rutile by means of re-heating at or above 1,000°C. The powder properties, however, deteriorate due to the progress of flocculation & sintering, and therefore, an attempt was made to directly generate rutile by means of a reaction.

Temperature & rutile conversion: The transition of titanium oxide into rutile becomes accelerated as the temperature rises, and therefore, the rutile conversion may be assumed to become upped as the reaction temperature rises. An attempt was therefore

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made to elevate the reaction temperature by elevating the reaction gas preheating temperature, and the concomitant rutile conversion variation was investigated. The results are shown in Fig. 5.

The reaction gas temperature was elevated to 1,100°C, which represents the upper limit of the preheater of the present apparatus. Although a rutile conversion gain tendency was observed in accordance with a reaction gas temperature gain, the gain was not conspicuous, and it was impossible to up the rutile internalization ratio to 75% or above.

Residing time & rutile conversion: The transition of titanium oxide into rutile should become facilitated as the residing time thereof within the reaction tube becomes prolonged at a high temperature. In Figure 2, the length of the reaction tube virtually coincides with the length L of the reaction zone, whereas the rutile conversion variation of a separate case where the residing time was prolonged by doubling the reaction tube length is shown in Figure 6. It was ascertained that the rutile conversion gain is miniscule even if the residing time is nearly doubled.

The concomitantly observed BET specific surface area and the variation, after a dispersion within an ultrasonic disperser, of the flocculated particle size as measured with a Coulter Counter are shown in Fig. 7. As the residing time becomes prolonged, the

flocculated particle size becomes enlarged, and the specific surface area becomes somewhat reduced. Figure 8 is a TEM microgram pertaining to a flocculated segment. It can be seen that particles have become mutually flocculated, resulting in the commencement of sintering. It may be surmised from these data that, once the reaction has reached an equilibrium, the generated powder should be immediately cooled instead of perpetuating the high temperature.

Addition of water vapor & rutile conversion: No significant rutile conversion gain is acknowledged even if such reaction conditions as the reaction temperature, residing time, etc. are changed. An attempt was therefore made to add a rutile accelerator. On occasions for manufacturing pigment-grade titanium oxides, various additives, led by aluminum trichloride, are added for purposes of accelerating the generation of rutile and of improving the pigment performances, although these additives are unusable in the present setting from the standpoint of synthesizing a high-purity product. The addition of water vapor, which exerts utterly no effects on the purity, alone was therefore investigated.

In a case where a small quantity of water vapor is added to oxygen within the reaction tube of Fig. 2, the rutile conversion

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becomes profusely improved. This trend is shown in Fig. 9. The oxygen excess ratio was hereby computed by also taking into account the oxygen content of water vapor. On this occasion, the color of the reaction flame changes from orange to red, whereas in a case where a 100% rutile is generated, a reaction becomes induced under the pervasion of a ruddy crimson flame. The titanium oxide thus generated bears a yellowish color at 200°C immediately after the collection thereof, although it bears a virtually pure white color tinted with an extremely pale creamy shade at normal temperature.

The reaction between water vapor & titanium tetrachloride is expressed by the following scheme:

$$TiCl_4 + 2H_2O \rightarrow TiO_2 + 4HCl \ldots (2)$$
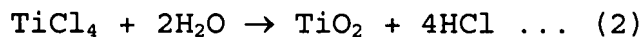
The relationship between the Gibbs' standard free energy ΔG' & temperature of this reaction is shown in Fig. 3. The reaction with titanium tetrachloride becomes accelerated far more effectively by water vapor than by oxygen at a high temperature. The crown-shaped deposits adhered to the distal end of a nozzle grow conspicuously as a result of the addition of water vapor in comparison with a case where a reaction is induced in the presence of oxygen alone. It can thus be surmised that the reaction rate of water vapor is higher and that, in a case where a titanium tetrachloride jetted from the nozzle becomes contacted with an

oxygen atmosphere inclusive of water vapor at a high temperature, the water vapor becomes reacted first & preferentially. As Fig. 9 indicates, the BET specific surface area also becomes enlarged as a result of the addition of water vapor, from which can be discerned that the water vapor also serves as a crystal nucleating agent on this occasion.

Generation of anatase: Next, conditions required for manufacturing pure anatase particles were investigated.

In a case where the $TiCl_4$ feeding rate is depleted without adding water vapor, the reaction temperature drops, and therefore, the rutile conversion tends to diminish, as in the case of the relationship with the reaction gas preheating temperature shown in Fig. [5?]. This relationship is shown in Fig. 10. Even if the $TiCl_4$ feeding rate is lowered to 50 kg/h, which is equivalent to the turbulent flow limit Re number of 2,300 within the reaction tube, the rutile conversion is lowered only to approximately 50%.

Attempts were then made not only to lower the $TiCl_4$ flow rate to 40 kg/h and, for purposes of perpetuating the turbulent flow state within the reaction tube by compensating for this flow rate and of inhibiting a reaction temperature gain, to up the oxygen excess ratio from 1.2 to 1.4 but also to lower the temperature for preheating these reaction gases from 1,000°C to 9[?]0°C, as a result of which the anatase internalization ratio was upped all

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the way to 100%. The color of the reaction flame concomitantly changed from yellow to yellowish green, whereas the product titanium oxide bore a slightly bluish though virtually pure white color. Absolutely no rutile

peak was observed in the course of X ray diffraction, and a titanium oxide bearing the peak of anatase alone was successfully obtained. Incidentally, the Re number within the reaction tube at this time was 2,500.

It can be gleaned from these results that, in a case where the reaction temperature drops below 1,000°C and approaches 9[?]0°C, the anatase internalization ratio rapidly increases. The

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reaction temperature was calculated in terms of a heat balance by taking into account the incoming heat ascribed to the reaction gases & outgoing heat ascribed to cooling water, etc. within the reaction tube as well as the reaction equilibrium. It has heretofore been deemed impossible to obtain a totally anatase crystal based on an industrial vapor phase oxidation method, whereas considering that the reaction temperature of the present conditions is low to the extent that it is difficult to perpetuate a combustion reaction and that the control range is also narrow due to the drastic rutile conversion variation in the vicinity of 900°C, it may be assumed that such reaction conditions are

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unachievable within an industrial apparatus of an excessively large scale.

It is assumed that, in the course of crystallization, anatase particles & rutile particles are grown respectively from anatase nuclei & rutile nuclei, and therefore, the designation of nucleating conditions in the course of the reaction may be presumed to represent the most important crystal control parameter. Although the transition of anatase particles into rutile particles in the course of growth within the reaction zone is not utterly non-existent, it is not predominant. At 1,000°C or higher, the transition of anatase into rutile should be extremely fast, although since a heat transmission rate-determining step exists during a transition experiment in which a powder is reheated, it was impossible to measure the transition rate due to the predominance of this factor. Even in such a case, however, the residing time does not serve as a dominant transition factor over a reaction period of 0.1 s or so. In a case where titanium tetrachloride & oxygen are reacted, the titanium oxide generated at 1,200°C or higher includes abundant rutile, whereas anatase becomes abundant at a lower temperature. In a case where water vapor is added as an agent for generating rutile nuclei on this occasion, the particle size becomes minimized, accompanied by a drastic rutile conversion gain, although these tendencies are also

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dependent on the temperature, and in a case where the reaction temperature is as low as 1,000°C or below, anatase becomes dominant even in the course of a water vapor reaction.

2.3. Particle size control

The particle size control of a case where the crystalline tissue is rutile was investigated. In a case where the Re numbers within the nozzle & reaction tube are upped with regard to the above-mentioned reaction tube shown in Fig. 2 and where reaction gases preheated at a high temperature are rapidly mixed & reacted, fine particles become obtained. In a case where the gases are fluidized as a laminar flow, on the other hand, fine particles & crude particles coexist within the obtained product, as has been demonstrated in the previous report, whereas such crude particles are assumed to have grown as a result of a slow reaction. An attempt was therefore made to generate homogeneous crude rutile particles by lowering the reaction rate to the extent that the above-mentioned three fundamental reaction conditions for generating homogeneous particles are satisfied.

Under such conditions, the reaction rate represents a turbulent flow diffusion rate-determining step, and therefore, the reaction rate is varied by varying this diffusion rate, which is tantamount to a particle size control measure.

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In a case where the generation of crude particles is targeted, the diffusion & mixing rate becomes decelerated by attenuating the reaction gas jetting rate & flow rate within the reaction tube. For realizing this goal, the nozzle diameter & reaction tube diameter were enlarged within production design limits. Since the reaction zone becomes prolonged in accordance with a reaction rate loss, the required reaction tube length becomes prolonged. Since the reaction tube length is prolonged, the rutile conversion becomes stabilized, and therefore, the addition of water vapor, which entails a particle size loss tendency, was executed somewhat conservatively.

Fig. 11 shows SEM micrograms of fine particles & crude particles thus obtained. Moreover, their reaction conditions & powder properties are compared & shown in Table 1. On this occasion, the length L of the reaction zone was calculated by using the formula shown in the previous report.

As a result, 100% rutile particles the sizes of which were at least doubly different, namely fine particles of 0.20 μm & crude particles of 0.52 μm, were successfully generated.

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A long-term continuous operation experiment was conducted under feeding conditions similar to those shown in Table 1 by using a water-cooled reaction tube made of graphite for the

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purpose of avoiding sedimentation. A graphite reaction tube bearing dimensions utterly identical to those of its counterpart of the previous report was used for the fine particles, whereas a tapered tube (inlet diameter: 140 mmφ; output diameter: 180 mmφ; total length: 1,000 mm) which had been divided into two via the 500 mm median thereof for facilitating handling was used for the crude particles. Within these reaction tubes, purge gases are also blown, and therefore, the powder properties somewhat deteriorate. Consistently obtained properties are shown in Table 2. Incidentally, the ignition loss (mainly water content) after dechlorination is proportional to the specific surface area within an open atmosphere.

2.4. Spherical particles

In a case where the titanium tetrachloride vapor exiting the evaporator was hydrolyzed at a high temperature with an oxyhydrogen flame, fine particles of 0.1 μm or less inclusive of abundant particles were obtained, although they were different from their counterparts obtained based on the oxygen vapor phase oxidation method. This method is being utilized as a method for manufacturing ultrafine particles of approximately 0.030 μm (Nippon Aerosol Co., 1985), whereas in a case where a titanium tetrachloride vapor is decomposed by using such an auxiliary

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combustion flame without heating the reaction gases, spherical particles inclusive of abundant anatase can be obtained, though for unknown reasons. The corresponding SEM microgram is shown in Fig. 12. The possibility of using this method for manufacturing spherical particles cannot be ruled out.

Conclusions

Attempts were made to control powder properties in the context of synthesizing high-purity titanium oxide based on the vapor phase oxidation method, as a result of which the following results were obtained:

1): It is necessary to induce a combustion reaction at the turbulent flow diffusion rate-determining step for the purpose of generating homogeneous particles, namely of generating particles homogeneous in terms of the crystalline tissues, particle sizes, & particle shapes of the respective primary particles, whereas the particle sizes were controlled between a fine particle size of 0.20 µm & a crude particle size of 0.52 µm by changing said diffusion rate and by designating a proportional reaction tube length.

2): From the standpoint of controlling the tissues of particles, a reaction temperature gain & a prolonged residing time alone are not sufficient for synthesizing pure rutile particles,

although the sought objective can be achieved by designating the preheating temperature at 1,000°C or above and by adding a small quantity of water vapor. It has been verified, on the other hand, that the anatase internalization ratio rapidly increases as the reaction temperature approaches 9?0°C. It has heretofore been deemed impossible to obtain a totally anatase crystal based on an industrial vapor phase oxidation method, although a 100% anatase was successfully obtained by lowering the reaction temperature by upping the oxygen excess ratio, etc.

These insights have affirmed the possibility of continuously producing, as an electronic ceramic feed material, a titanium oxide powder which is high in purity & homogeneous and bears a singular crystalline tissue wherein flocculation is inhibited & a particle size suitable for a targeted application.